

# FIELD IONIZATION MASS SPECTROMETRIC ANALYSIS OF SEDIMENTS FROM DIESELS DOPED WITH STRONG ACIDS

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## ABSTRACT

Filtered sediments formed in Texas diesel containing light cycle oil under ambient conditions and upon accelerated ageing at 80 °C for two weeks with added dodecylbenzenesulfonic acid (DBSA) or chloroacetic acid were examined by pyrolysis-field ionization mass spectrometry (Py-FIMS). During the analysis over 50% of the sediment was devolatilized. The spectra showed very similar profiles and correspondence between most prominent peaks indicating that doping with these acids does not drastically alter the chemistry of sediment formation, but merely accelerates the natural ageing. Sediments formed under accelerated ageing of the diesel doped with *p*-*t*-butylthiophenol again showed a similar spectrum as well as peaks for the oxidized products of the dopant, namely di-*p*-*t*-butylphenyl disulfide and *p*-*t*-butylbenzenesulfonic acid, thereby supporting the suggestion that sediment formation is an acid-catalyzed process and that sulfonic acids or other acids are formed by autoxidation of the fuel. Py-FIMS analysis of the adherent gum formed in the thiol-doped fuel gave a spectrum almost identical to that of the filtered sediment confirming their similar chemical nature.

## INTRODUCTION

Storage of fuels often results in the formation of deposits that cause problems with filtration and pumping of the fuels. Furthermore, some soluble gum is also formed that subsequently forms deposits on the hot engine parts causing additional problems. Numerous tests have been developed to predict the tendency of a fuel to form deposits.(1) Often, these tests require stressing the fuel at elevated temperatures, and the relevancy of such tests to storage conditions is not clear. Studies have also been conducted with dopants (2, 3), but again it is unclear whether the deposits formed in the presence of the dopant are the same as those formed under storage. An improved chemical understanding of the nature and causes of deposit formation is clearly needed. Chemical characterization of the sediments is valuable, because the agents responsible for their formation may be present at extremely low concentration in the fuel, but will necessarily be concentrated in the sediments.

We have previously shown that pyrolysis-field ionization mass spectrometry (Py-FIMS) is very useful in characterizing the deposits formed during storage of fuels.(4,5) We have found that there are a few patterns that repeat in the spectra for sediments from a variety of sources and that the filtered sediments and adherent insoluble gums are very similar in chemical nature with the sediments being enriched in the benzologs of the components in the gum. We also showed that sediments from fuels with dopants such as 2,5-dimethylpyrrole (DMP) are completely different from that observed for undoped fuels; the sediment was largely comprised of DMP-derived materials. This result illustrates the possible dangers associated with studying accelerated aging using dopants and the need to characterize the sediments to ensure that the chemistry being examined is relevant to the native system.

We now wish to report results obtained from a variety of deposits obtained with fuels doped with strong acids or their precursors. The accompanying paper by Hazlett and Schreifels

(6) describes the aging experiments and the analysis of sediments by other techniques, such as titration with alkali and XPS, while this paper focuses on the analysis of the deposits by Py-FIMS.

## EXPERIMENTAL

**Accelerated Aging.** A 20/80 blend of a light cycle oil with straight run diesel was aged at 80°C for 7 (or 14) days. Insoluble sediment formed in the fuel under ambient storage was also examined as an appropriate control. The dopants used in this study were: (1) a sample of dodecylbenzenesulfonic acid (DBSA), (2) *p*-t-butylthiophenol (PBTP), and (3) chloroacetic acid. The sediments were collected by filtration through glass fiber filters and the adherent gums were dissolved in a 1:1:1 (vol) mixture of toluene, acetone, and methanol, transferred to a small vial and the solvent evaporated.

**Pyrolysis/Field Ionization Mass Spectrometry (Py/FIMS).** The technique of field ionization (FI) consists of passing vapors of the material to be analyzed through a region of intense electric field.(7) This mild technique for ionization results in the formation of only the molecular ions for most compounds, and its nonfragmenting nature makes it particularly useful for analyzing complex mixtures. The FIMS system used in this study has been described elsewhere.(8) It consists of an activated tantalum foil field ionizer interfaced with a 60° magnetic sector mass analyzer and a PDP 11/23 computer for data acquisition and processing. Approximately 50 µg of the sample is introduced via a heatable direct insertion probe. Mass spectral data of the evolving volatiles are collected by repeatedly scanning the magnet over a preset range while the sample is gradually heated from the initial temperature (sometimes as low as -78°C) to approximately 500°C. At the end of the run, the sample holder is retrieved and weighed to determine the fraction that was devolatilized during the analysis. All the samples examined in this study were devolatilized to about 60% during analysis. For a given sample, many spectra are collected, each representing a certain range of temperature. The individual spectra are added to obtain a spectrum of the total volatiles and produce a thermal evolution profile of total volatiles as well as of any given mass peak.

## RESULTS AND DISCUSSION

The Py-FIMS analysis of the adherent gum from ambient aging of the fuel gave the spectrum shown in Figure 1. It shows the characteristic groups of peaks corresponding to monomers, dimers, and trimers extending over the mass range 100 to 700 amu. The spectrum contains major peaks at *m/z* 131, 145, and 159. These features are in accord with those found in our previous investigations.(4,5) The peaks at *m/z* 131, 145, and 159 have been assigned to methylindole and its homologs (9-11).

**Effect of Dodecylbenzenesulfonic Acid.** Figure 2 shows the Py-FIMS of the filtered sediment formed upon stressing the fuel at 80°C for 7 days with DBSA as a dopant. The most intense peaks are seen at *m/z* 298, 312, and 326. Parent ion due to DBSA would appear at *m/z* 326, and we were puzzled to see the peaks at 312 and 298, which correspond to successive loss of methylene. The FI-mass spectrum of the DBSA sample also gave the peaks at *m/z* 312 and 298 in addition to the peak at *m/z* 326 and it appears that the particular sample of dodecylbenzenesulfonic is actually a mixture decyl-, undecyl-, and dodecyl- benzenesulfonic acids. The Py-FIMS of the deposit gave peaks at *m/z* 131, 145, and 159 and shows the general features of filtered sediments from undoped fuels (5) including relatively prominent peaks at *m/z* 181, 195, and 209 corresponding to the benzologs of methylindole and its homologs. On the basis of this information, we can surmise that DBSA does not drastically alter the chemistry of sediment formation but promotes the reactions that occur in undoped sediments. To the extent that DBSA is seen in the sediments as a prominent constituent, it must also contribute to insolubles formation. Whether this DBSA is present in the insolubles merely due to adduction or due to the formation of insoluble salts cannot be discerned at present.

**Effect of *p*-t-butylthiophenol.** Py-FIMS of the sediment obtained from doping the fuel with PBTP is shown in Figure 3. The spectrum is similar to the one for the sediment from the DBSA-doped fuel except that instead of the peaks due to the DBSA sample there are prominent peaks at *m/z* 166, 214, and 330. The peak at *m/z* 166 corresponds to PBTP itself and that at 330 to the corresponding disulfide, an expected product of oxidation. The peak at *m/z* 214 corresponds to *p*-t-butylbenzenesulfonic acid, and this observation lends support to the hypothesis that insolubles formed during storage are a result of acid-catalyzed chemistry, and that the acids are

themselves a product of autoxidation.(6) There is an additional prominent peak at  $m/z$  185, which remains a mystery.

**Effect of Chloroacetic Acid.** Once again, the Py-FIMS of the sediment from the fuel doped with chloroacetic acid displays general features similar to those for the other sediments. Peaks due to chloroacetic acid ( $m/z$  94 and 96) are absent and it appears that this acid is not adducted into the insoluble sediment. The absence of chloroacetic acid in the sediment would also suggest that salt formation is probably not the reason for the presence of other acids in the sediments, however, Cl was detected in the sediment by XPS (6) and we cannot draw any firm conclusions regarding the mechanism of dopant adduction at the present moment.

## CONCLUSION

Pyrolysis-FIMS is a useful technique for characterizing fuel deposits. In this study, we showed that the nature of the deposits formed by doping the fuel with DBSA or chloroacetic acid is similar to that formed in undoped sediments. Substantial amounts of the deposits were devolatilized during the analysis ensuring that the data do not result from an insignificant part of the deposit. Oxidation of *p*-*t*-butylthiophenol results in the formation of *o*/*p*-*t*-butylbenzenesulfonic acid in addition to the disulfide. The sulfonic acid then catalyzes formation of insolubles.

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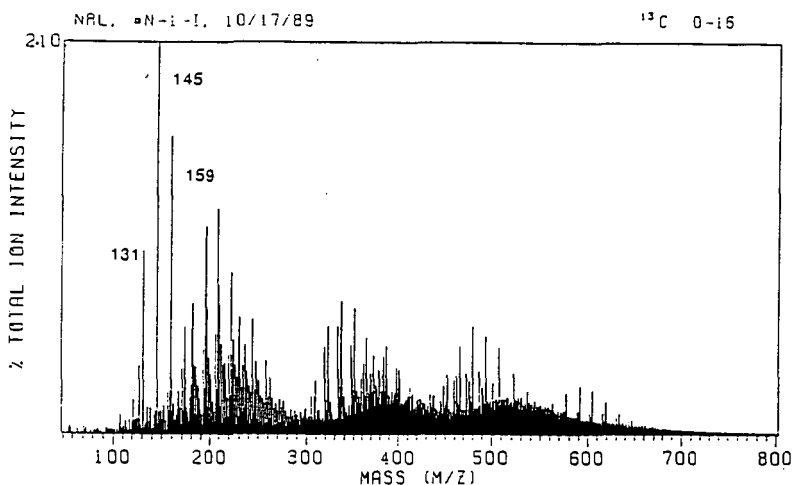


Figure 1. Py-FIMS of insoluble adherent gum from ambient aging of a 20/80 blend of light cycle oil and straight-run diesel.

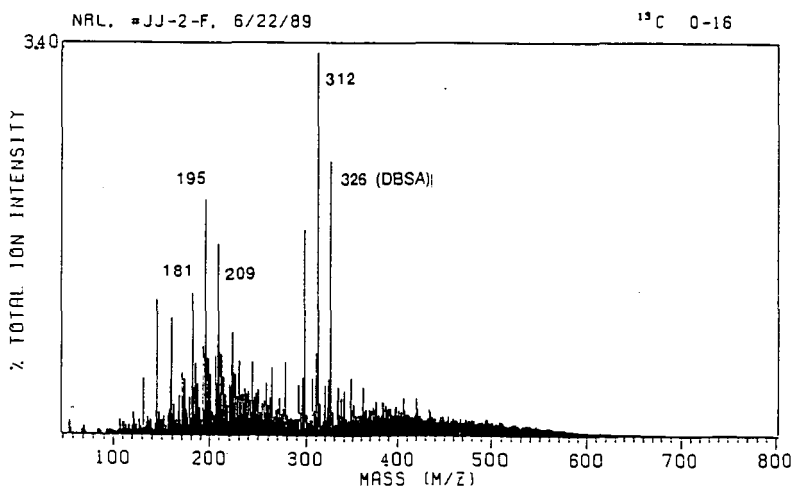


Figure 2. Py-FIMS of filtered sediment from accelerated aging at 80°C for 7 days of a 20/80 blend of light cycle oil and straight-run diesel doped with dodecylbenzenesulfonic acid.

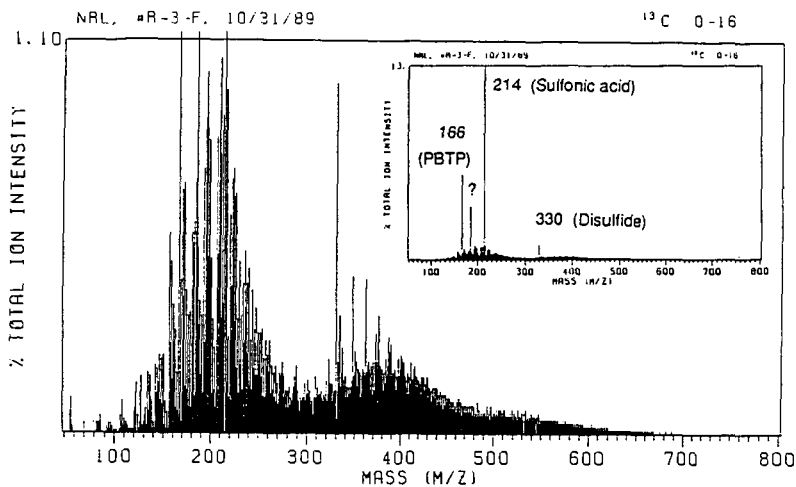


Figure 3. Py-FIMS of filtered sediment from accelerated aging at 80°C for 7 days of a 20/80 blend of light cycle oil and straight-run diesel doped with *p*-t-butythiophenol. (Inset: Same spectrum with increased vertical scale.)

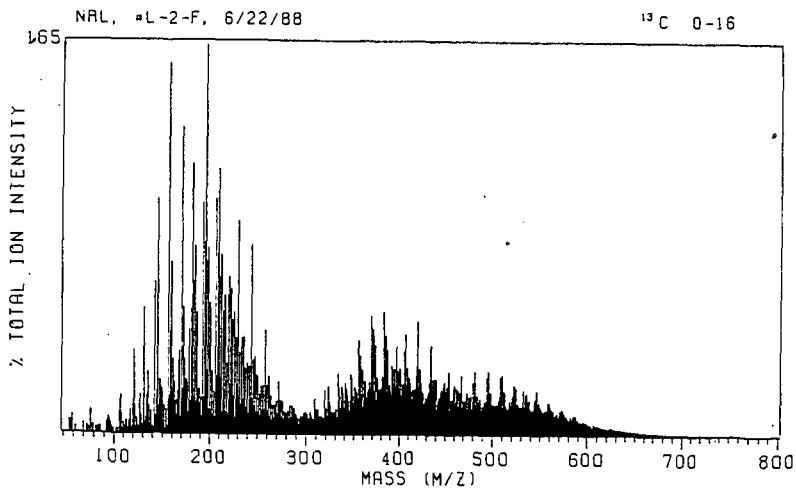


Figure 4. Py-FIMS of filtered sediment from accelerated aging at 80°C for 7 days of a 20/80 blend of light cycle oil and straight-run diesel doped with chloroacetic acid.